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THE CONTROVERSIAL FORMATION OF ELEMENTAL FLUORINE IN A CHEMICAL PROCESS*

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SUMMARY

Five years before Moissan prepared elemental fluorine by electrolysis, elemental fluorine was obtained by Brauner in thermal decomposition of lead tetrafluoride and cerium tetrafluoride and their complex salts. His experiments were not fully duplicated. The controversies in the chemical method of the preparation of fluorine will be discussed.

INTRODUCTION

In 1881, B. Brauner claimed that he obtained elemental fluorine by thermal decomposition of lead and cerium tetrafluorides and their complex salts with potassium fluoride [1]. His experiments were not duplicated in full extent either by O. Ruff [2] or by W. L. Argo *et al.* [3]. Later (1916) Brauner admitted that, although he proved the presence of fluorine qualitatively by ignition of silicon, a quantitative proof was lacking [4]. A more detailed summary of the preparation of fluorine by thermal decomposition of high valence fluorides has been published recently [5].

RESULTS

Encouraged by Dr. W. T. Miller, Jr., I repeated Argo's *et al.* experiments on thermal decomposition of a mixture of lead dioxide and potassium hydrogen fluoride [3]. I did not obtain even traces of elemental fluorine, but found a considerable quantity of green nickel fluoride in the solid residue after the reaction in the stainless steel vessel. Evidently the nickel, a component of the stainless steel used, reacted with fluorine as it was evolved on heating of the lead tetrafluoride to a red glow.

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However, it is not impossible that the nickel fluoride resulted from the reaction of the stainless steel with the molten salt containing lead tetrafluoride and potassium fluoride. Under similar conditions, platinum reacted with hydrogen tripotassium lead octafluoride to form dipotassium platinum hexafluoride [6].

EXPERIMENTAL

The preparation as well as the decomposition of ternary lead tetrafluoride were carried out in a 30 ml stainless steel cylinder (Hoke, 4H SY 30) fitted with a type 304 stainless steel T-assembly (Whitey, swage lock valve). The tube reaching approximately 1.5 cm above the bottom of the cylinder was used for the introduction of argon which was passed in a gentle current through the apparatus during the entire operation. The other end of the T-assembly was connected to a glass bubbler filled with a dilute solution of sodium iodide acidified with hydrochloric acid and containing starch as the indicator.

Potassium hydrogen fluoride (99+%, Alfa Products) was ground and dried at 140-150°C for 40 hours, and was allowed to cool in a desiccator over phosphorus pentoxide. Lead dioxide (extra pure, EM Science, Germany) was stored over phosphorus pentoxide.

In a representative experiment carried out according to reference [3], 2.14 g (0.0274 mol, 4 equiv.) of potassium hydrogen fluoride and 1.64 g (0.00685 mol) of lead dioxide were thoroughly mixed in a small beaker and immediately transferred into the steel cylinder. The T-assembly was screwed in and a slow stream of argon was passed through the apparatus to expel the air. The cylinder was heated gently with a Bunsen burner for about 15 minutes; the heat was increased until the cylinder began to glow red (within 1 hour). During the experiment not a trace of fluorine escaped from the apparatus. After cooling in the stream of argon, the apparatus was disassembled and the cylinder was emptied. From 3.49 g of the greyish residue, 0.45 g of pure light green material was separated mechanically. It was most probably the tetrahydrate of nickel difluoride [7] resulting from the fluorination of nickel contained in the stainless steel.

A portion of the green compound was dissolved in a minimum amount of warm water (50°C), the solution was filtered and evaporated under reduced pressure. A yellow solid was dissolved in dilute aqueous ammonia, a brown precipitate of ferric hydroxide was filtered off, and the filtrate was treated with dimethyl glyoxime. A pink precipitate of the nickel compound was isolated by filtration.

CONCLUSIONS

The discrepancies among the findings of different authors are most probably due to non-identical experimental conditions, especially with respect to temperature. At two different temperatures within the 'red glow' range elemental fluorine could have been generated, but could also have immediately reacted with the metal of the apparatus such as platinum or stainless steel. Platinum tetrafluoride and nickel difluoride, respectively, were indeed found in the reaction residues.

The first unequivocal preparation of elemental fluorine by a chemical method was achieved by K. O. Christie by heating dipotassium hexafluoromanganate with antimony pentafluoride. It was reported at the International Symposium, 'Centenary of the Isolation of Fluorine,' in Paris, August 25-29, 1986, and described in Chemical and Engineering News, 1986, 64 (37) 23.

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